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## **Development of Novel Polynitrogen-based High-performance Solid Propellants**

### **STTR Phase I Final Report**

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## EXECUTIVE SUMMARY

Solid propellants are widely used in propulsion systems, as it does not require complicated engine design. They are primarily used in to space vehicles, strategic and tactical missile systems. The mission of Air Force and, in general, DoD is to develop novel high energy propellant ingredient for next generation solid propulsion systems. Recently several high energy polyazide compounds have been synthesized. However, these compounds suffer several drawbacks that prevent their practical use as propellant ingredients. Under this Phase I STTR program, CFDRRC, in collaboration with the University of Idaho, has shown the proof-of-concept via synthesizing and characterizing several high energy density compounds that have high potential for use as propellant ingredients. These compounds are derivatives of amino substituted tetrazoles.

CFDRRC first selected a number of compounds and performed theoretical calculations to evaluate their physical and chemical properties. These include heats of formation, densities, specific impulses, detonation pressures and velocities. The compounds were further screened for anticipated number of steps required and level of difficulty for synthesis. Such investigation reduced the time and cost of development. Seven energetic compounds were synthesized and characterized in the laboratory, and five of them found to have high potential for use as propellant ingredients. Some of these compounds have remarkably low impact sensitivities (lower than HMX and RDX) and high densities. The sensitivities were also measured in a mixture with varying percentage of ammonium nitrate. It is concluded that these compounds can be used with low percentage of ammonium nitrate to compensate the oxygen balance.

In a parallel task, we also initiated the development of a neural network based model for prediction of sensitivities. Our objective is to develop a unified model that would predict the sensitivity irrespective of the chemical class and composition of a compound. To our knowledge, all models, so far reported, use different equations for different classes of compounds. Successful development of such unified model will enable another important screening tool and prevent failure at the later stages of development. In Phase I, CFDRRC has shown a proof-of-concept by taking 45 molecules from different classes and used them to construct a preliminary network.

In Phase II, these compounds will be formulated, and undergo a rigorous set of tests, such as burn rate, compatibility, mechanical strength, to evaluate their performance in practical situations. The preliminary neural network model will be extended and fine tuned with a large number of input data, including salts.



## 1 INTRODUCTION

Solid propellants comprise one of the most widely used classes of propellants for propulsion systems. Unlike liquid propellants, solid propulsion systems require no complicated engines or plumbing, and only rely on strong casings to withstand pressure. Currently they are routinely used to launch space vehicles, strategic and tactical missile systems. Designing new high performance solid propellants with desired physical and chemical properties is a challenge. Several physical and chemical properties must be satisfied simultaneously. In addition, the propellant must possess acceptable hazard, mechanical and processing properties, and should be able to integrate within existing infrastructures with minor or no modification. An ideal solid propellant should have, at least, the following properties: a) high energy content (heat of formation); b) low sensitivity towards to mechanical and thermal shock, and electrostatic discharge; c) high density; d) high specific impulse, and e) good oxygen balance.

In recent times, polynitrogen compounds have attracted much attention due to their high nitrogen content which results in high energy content.<sup>1-3</sup> Among polynitrogen compounds, polyazides have gained particular interest, because they contain multiple high-energy azide functionalities ( $-N_3$ ). Although these compounds are indeed energetic, they suffer from the following serious drawbacks.

In order to obtain a neutral or anionic species with a large number of azide substituents, it is necessary to select a central element that is capable of exhibiting a high positive oxidation number. Typically, the central element is a transition metal of sufficiently large size to coordinate several azide groups. Unfortunately the neutral polyazide species, e. g.,  $M(N_3)_6$  [ $M = Mo$  (molybdenum) or  $W$  (tungsten)], are extremely sensitive even at low temperature. However, dianionic heptaazides  $M'(N_3)_7^{2-}$  [ $M' = Nb$  (niobium), or  $Ta$  (tantalum)] can be stabilized when combined with a large cation,  $[P(C_6H_5)_4]^+$ .<sup>2</sup> The type of salts formed by this combination is  $\{[P(C_6H_5)_4]^+ M'(N_3)_7^{2-}\}$ . The stability of these salts is barely sufficient for X-ray structure determination. The improved stability (compared to  $M(N_3)_6$ ) is likely due to the presence of the large cations. However, the presence of the high molecular weight cations reduces the energy density drastically, and thereby suppresses the detonation propagation. In addition, the presence of heavy metals and large cations gives rise to a marked decrease in the densities of these salts. Density is a very important characteristic in building species with desirable energetic properties (high detonation pressure and velocity and maximum specific impulse). These polyazide salts have densities around only  $1.5 \text{ gm/cm}^3$  which is considerably smaller than ammonium nitrate ( $1.7 \text{ gm/cm}^3$ ), a common propellant ingredient. They also have very low oxygen balance (for example, -138 for  $[P(C_6H_5)_4]^+ M'(N_3)_7^{2-}$  with  $M' = Nb$ ) which indicates that the performance will deteriorate due to lack of oxygen, because the elements will not be fully converted to their oxides during combustion. Additionally, although their hydrolytic stabilities have not been reported, it is likely that these polyazides are extremely water sensitive given the anhydrous synthesis conditions employed. Therefore, in view of their low stabilities, extreme shock and impact sensitivities, low densities, and anticipated hydrolytic instabilities, such polyazides are unlikely to be suitable for use as stable, dependable solid propellants.

Based on the limitations mentioned above, the practical value of polyazide compounds as solid propellant remains questionable. In this STTR, CFDRC and Professor Jean'ne M. Shreeve of the University of Idaho have teamed up to develop tetrazole-based polynitrogen salts that will overcome the problems associated with polyazides. A number of compounds have been synthesized and found to have high energy density and low sensitivity, and are concluded to have excellent potential for next generation energetic materials.

Recently nitrogen-rich five-membered heterocyclic compounds have been shown to have significant promise as high energy density materials, primarily due to the excellent research performed independently by the groups of Klapötke<sup>4</sup> and Shreeve.<sup>5</sup> Figure 1 shows a few heterocyclic nitrogen-rich compounds. Additional stability of these compounds arises due to the  $\pi$  aromatic delocalization in the ring, in contrast to the acyclic polyazides. The important properties of these heterocycles can be further enhanced by converting them to salts.

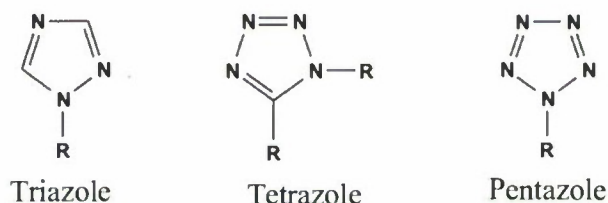


Figure 1. Neutral Heterocyclic Compounds. *R* is the Substituent Group

In this STTR proposal, we have combined the tetrazole based cationic form (tetrazolium ion, Figure 2) with various energetic anions to enhance the energy density, stability and oxygen balance. We selected the tetrazole-based cation because pentazole, although having high energy content, is very sensitive and unstable. On the other hand, triazole is stable, but has lower energy content than tetrazole. Therefore tetrazole offers a good trade-off between energy content and stability. The energy density of tetrazole and its cation can be further enhanced when the substituent group(s) is amine ( $\text{NH}_2$ ) giving rise to 1,5 diaminotetrazole (DAT) and 1,5 diaminotetrazolium cation (HDAT), respectively. Also, the ability of the  $-\text{NH}_2$  group to form hydrogen bonds leads to an enhanced density. In addition, DAT has a high heat of formation and high thermal stability which makes it an excellent precursor of high energy density materials.



Figure 2. (a) Tetrazolium Cation Combined with an Anion *X* an Energetic Anion; (b) 1,5 Diaminotetrazolium Cation (HDAT) Combined with Anion *X*



Sensitivity is one of the most important properties of an energetic material. The material must be insensitive to impact, friction and electrostatic charge. Unlike, heat of formation, density and specific impulse, there is no reliable method for prediction of sensitivity. Therefore, we have initiated the development of a model for sensitivity prediction. Full development of such model would eliminate the materials that are too sensitive at the earliest stages of their development.

## **2 PHASE I ACCOMPLISHMENTS**

At the end of Phase I, all tasks proposed originally have been successfully completed. Following are the highlights of the accomplishments:

- A number of energetic polynitrogen solids have been considered. Most of them are tetrazole based salts.
- The properties, such as heats of formation, densities, specific impulses, density impulses, detonation velocities and pressures have been computed/estimated using well established techniques, such as quantum chemical and thermo chemical methods.
- Several salts have been considered for synthesis based on computed properties. Their densities, melting and decomposition temperatures, and impact sensitivities have been determined in the laboratory.
- Impact sensitivities of the promising candidates were measured with varying percentages of ammonium nitrate (AN) to examine the change in their sensitivities.
- A preliminary model based on Artificial Neural Network (ANN) has been developed for prediction of impact sensitivity.

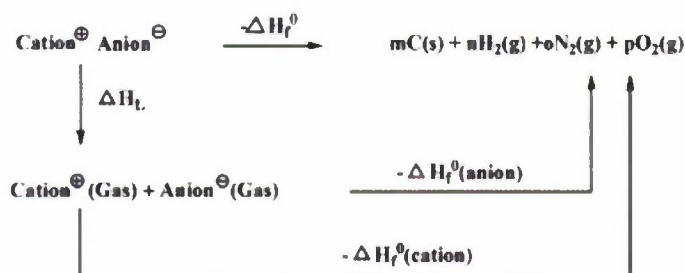
## **3 PHASE I RESULTS**

Under this section, we first outline the theoretical methods that have been used to compute/estimate the properties. We then describe the results obtained using these methods, and the compounds that are selected for synthesis. The synthesized compounds were then characterized. The results of laboratory measurements will be reported. Finally a preliminary ANN model for predicting impact sensitivity will be discussed.

### **3.1 Methods of Property Estimation**

#### **Heat of Formation**

Heat of formation (HoF) is the most important parameter to be considered when designing an energetic material, because it is directly related to the specific impulse. We use the following Born-Haber cycle to compute the HoF of the solid salts.



where  $\Delta H_L$  is the lattice energy of the salt. The heat of formation of the salt can be computed as the following:

$$\Delta H_f^0(\text{ionic salt}, 298K) = \Delta H_f^0(\text{cation}, \text{gas}, 298K) + \Delta H_f^0(\text{anion}, \text{gas}, 298K) - \Delta H_L \quad (1)$$

As can be seen, the heats of formation for anions and cations in the gas phase should be computed separately. Currently, *ab initio* quantum chemistry is the most accurate method for computing heats of formation in the gas phase. For this work, we optimize the geometry at the 6-31+(d,p) level with B3LYP exchange-correlation functional using Gaussian 98 program package. Single point energy calculations were then performed at the MP2(full)/6-311++G(d,p) with the optimized geometries. The procedure followed in Gaussian 98 is shown in Figure 3.

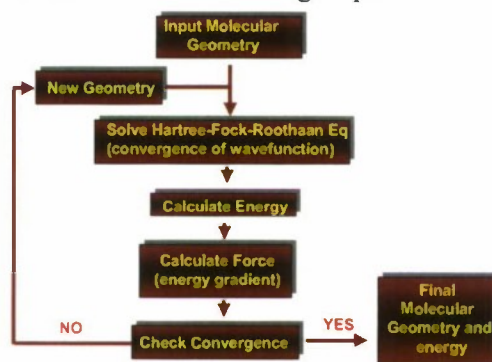


Figure 3. The Steps Involved in Quantum Chemical Calculation using the Gaussian Program

The lattice energy,  $\Delta H_L$ , has been calculated using the method described by Jenkins et al.<sup>6</sup> For a salt with general formula  $M_pX_q$ , the expression for lattice energy is given by:

$$\Delta H_L = U_{POT} + \left[ p \left( \frac{n_M}{2} - 2 \right) + q \left( \frac{n_X}{2} - 2 \right) \right] RT \quad (2)$$

where  $n_M$  and  $n_X$  are the numbers that depend on the nature of the ions  $M^{q+}$  and  $X^{p-}$  and are given in the paper by Jenkins et al.  $U_{POT}$  is defined as

$$U_{POT} = \gamma(\rho / MW)^{\frac{1}{3}} + \delta \quad (3)$$

where  $\rho$  and  $MW$  are the density and molecular weight of the salt, and  $\gamma$  and  $\delta$  are the two constants given by Jenkins et al.<sup>6</sup> The density of the salts can be estimated by a group contribution technique as described in the next section. Using equations (1), (2) and (3), one can obtain heats of formation of the salts in the solid state.

### **Density Estimation**

Densities have been estimated using the molecular volumes. The molecular volumes of the anions and cations were estimated by recently developed group contribution techniques by Professor Jean'ne Shreeve's group.<sup>7</sup> In this method, the volumes of many functional groups that are commonly found in organic chemistry are established. The total molecular volume of an anion or cations can be estimated as the following:

$$V_i = \sum_j N_{ij} O_j \quad (4)$$

where  $V_i$  is the volume of cation or anion,  $N_{ij}$  is the number of "j" type group in cation or anion "i", and  $O_j$  is the volume contribution of group "j". The total volume of the salt is given by:

$$V_T = \sum_i n_i V_i \quad (5)$$

where  $n_i$  refers to the number of anions and cations of type "i". The density calculated as:

$$\text{Density} = \frac{MW}{0.6022 \cdot V_T} \quad (6)$$

The densities of many salts and ionic liquids have been estimated by this method. The mean average deviation is found to be only 0.035 gm/cc. Therefore this method is accurate enough for prediction of densities for screening purposes.

### **Oxygen Balance**

Oxygen balance (OB) has been estimated using the following equation:

$$OB = \frac{-1600}{MW} \times (2X + \frac{Y}{2} + M - Z) \quad (7)$$

where X, Y, M and Z are the numbers of C, H, metal and O atoms in the molecule. A negative number signifies that the propellant is deficient in oxygen content. The low oxygen balance compounds can have deteriorated performance due to incomplete conversion of the carbons, hydrogens and metal atoms to their oxides.

### **Specific Impulse, Detonation Velocity and Pressure**

The estimated heats of formation and densities of the candidate salts have been used in the thermodynamic code, CHEETAH<sup>8</sup>, to compute specific impulse, and detonation pressure and velocity. These quantities are the measurement of the performance of an energetic material. The method followed in the CHEETAH is based on thermodynamic equilibrium, where a large number of product species have been considered for equilibrium calculations. Either pure material or a mixture of multiple materials can be used for specific impulse, detonation velocities



and pressure calculation. The detail discussion of the procedure is out of the scope of this report, but can be found in the user manual of CHEETAH.

### 3.2 Candidate Compounds, Synthesis and Their Properties

Following are the molecules selected initially for evaluation. All salts are named with a prefix "DAT".

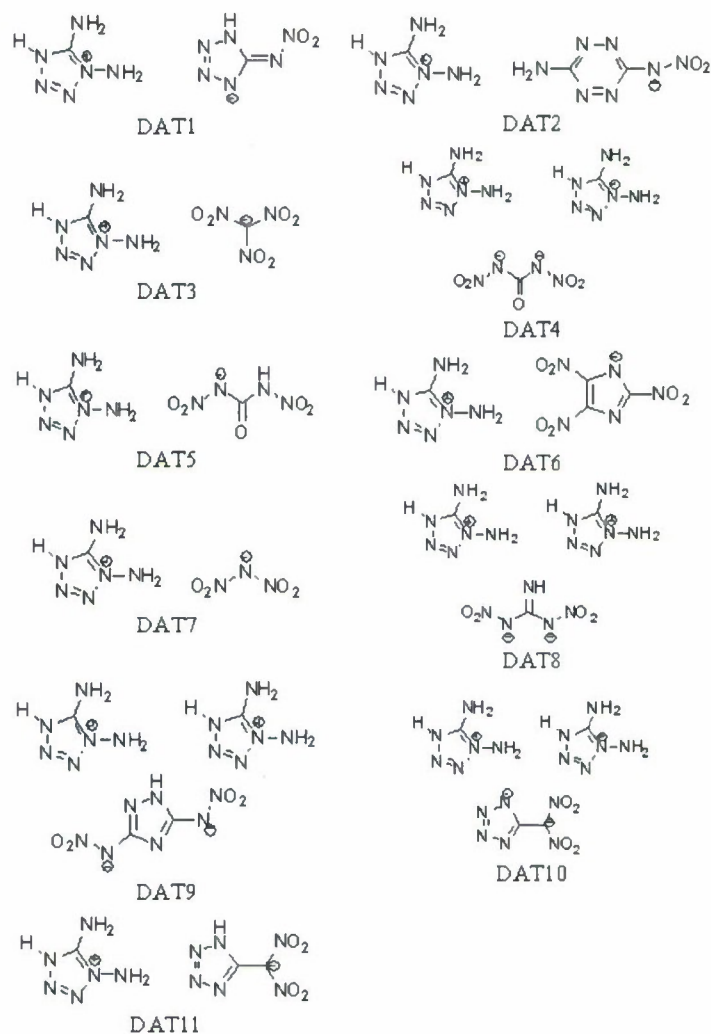


Figure 4. Initial Candidates for Property Estimation

The estimated properties of the salts are shown in Table 1. The heats of formation of two compounds, DAT7 and DAT8 could not be obtained at this time.

Table 1 Theoretical Computed/estimated Properties of the Proposed Salts Shown in Figure 1

Salts	Heat of formation (kJ/mol)	Calc. Density (gm/cc)	Oxygen Balance (%)	Isp (sec)
DAT1	555.8	1.721	-34.8	232
DAT2	828.7	1.614	-46.7	243.8
DAT3	266.6	1.774	-3.2	272.5
DAT4	857.9	1.741	-27.4	265.2
DAT5	352.5	1.798	-12.8	269.5
DAT6	418.0	1.798	-23.8	254.0
DAT7	370.7	1.791	-3.9	277.4
DAT8	*	1.725	-34.4	*
DAT9	*	1.697	-39.0	*
DAT10	1102.8	1.68	-40.6	251.9
DAT11	638.0	1.72	-29.2	256.4

\*could not be obtained at this time

All of the above compounds have positive heats of formation, and most of the compounds have high specific impulse. We also calculated density impulse (specific impulse x density) with varying percentages of ammonium nitrate (AN). The salts with very low oxygen balance perform worst when the percent of AN is reduced. This is due the fact that they do not possess enough oxygen for complete combustion. Although most of the salts looks quite good from theoretical calculations, their synthesis may be difficult. We therefore further investigated the compounds from the point of view of ease of synthesis. This is done by our university partner Professor Jean'ne M Shreeve who is an expert in synthesis of energetic materials.

Table 2. Evaluation of the Compounds Based on the Synthesis Difficulty

Salt	Synthesis Difficulty Prediction	Decision
DAT1	Generally good properties. Synthetic steps may be reasonable, but does not have performance beyond its mixture percent of 20%	Discarded
DAT2	Anion requires five steps; large negative oxygen balance, low density.	Discarded
DAT3	The trinitramide salts have low thermal decomposition temperatures.	Discarded
DAT4	Probably not possible to synthesize based on the low basicity of DAT	Discarded
DAT5	Synthesis may be difficult – compound unknown but could probably be synthesized – solubility problems. Impact sensitivity may be high.	Considered
DAT6	2,4,5-trinitroimidazole has a very long preparation.	Discarded
DAT7	A great compound, easy to make but has an impact sensitivity < 2 J. Klapotke has synthesized this.	Discarded
DAT8	Not possible to make, we believe, because of low basicity of DAT	Discarded
DAT9	Not possible to make, we believe, because of low basicity of DAT	Discarded
DAT10	Not possible to make, we believe, because of low basicity of DAT	Discarded
DAT11	An unknown compound but should be possible. Anion is three-step preparation.	Considered

From the above table, we considered DAT5 and DAT11 for synthesis. However, synthesis of DAT5 failed while DAT11 was successfully synthesized. Melting point and thermal stability measurements are carried out using DSC and TGA equipment. The density of solids is measured with a Micromeritics Accupyc 1330 gas pycnometer. A BAM Fallhammer apparatus is utilized for sensitivity measurements. The synthesis yield of DAT11 found to be only 10%-20% which is unacceptable, and also has high impact sensitivity

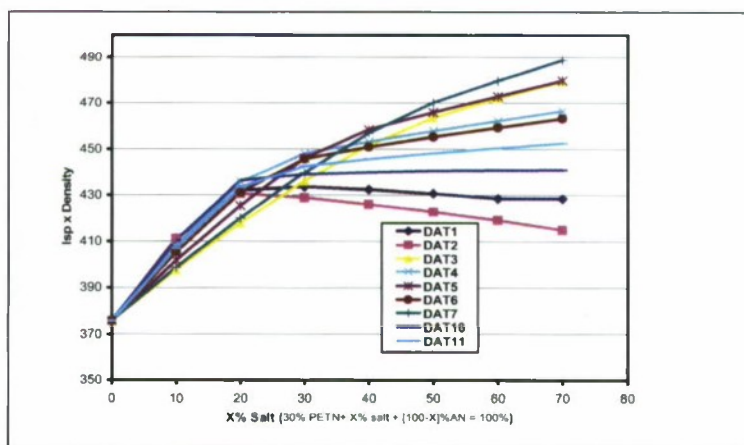


Figure 5. Density Impulses of the Salts at Different Formulation



We therefore searched for additional compounds. We selected few other compounds from a recent work by the group of our STTR partner, Professor Jean'ne Shreeve.

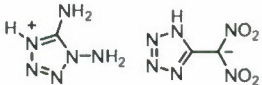
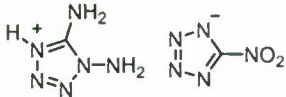
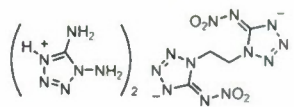
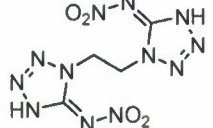
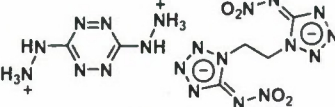
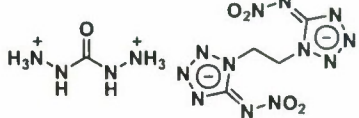
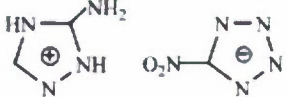
 <p><b>DAT11</b>  <b>Highly sensitive (&lt;4J)</b>  <b>Very low synthesis yield</b></p>	 <p><b>DAT12</b>  <b>Highly sensitive (&lt;1J)</b>  Isp = 249sec, Density = 1.71g/cc  Pressure = 30.69 GPa  Velocity = 8843 m/s  Melting point = 128 °C  <b>High synthesis yield</b></p>	 <p><b>DAT13</b>  <b>Low sensitive (10J)</b>  Isp = 255sec, Density = 1.7g/cc  Pressure = 30.68 GPa  Velocity = 8904 m/s  Melting point = 174 °C  <b>High synthesis yield</b></p>
<p><b>Not considered</b></p>	<p><b>Sensitivity with 80% AN=38J</b></p>	<p><b>Sensitivity with 80% AN=30J</b></p>
 <p><b>DAT14</b>  <b>Low sensitive (10J)</b>  Isp = 276sec  Density = 1.858g/cc  Pressure = 37.52 GPa  Velocity = 9198m/s  Melting point = 194 °C  <b>High synthesis yield</b></p>	 <p><b>DAT15</b>  <b>Low sensitive = 9 J</b>  Isp = 238.89 sec  Density = 1.82 g/cc  Pressure = 33.97 GPa  Velocity = 9222 m/s  Melting point = 203 °C</p>	 <p><b>DAT16</b>  <b>Low sensitive = 8 J</b>  Isp = 259.30 sec,  Density = 1.722 g/cc  Pressure = 31.42 GPa  Velocity = 8840 m/s  Melting point = 203 °C</p>
<p><b>Sensitivity with 80% AN=22J</b></p>	<p><b>Sensitivity with 80% AN=40J</b></p>	<p><b>Sensitivity with 80% AN=45J</b></p>
 <p><b>DAT17</b>  <b>Very Low sensitive = 56 J</b>  Isp = 246.02 sec  Density = 1.75 g/cc  Pressure = 31.42 GPa  Velocity = 8843 m/s  Melting point = 159 °C  <b>High synthesis yield</b></p>	<p><i>Figure 6. The Tetrazole-based Polynitrogen Compounds that have been Synthesized and Characterized. All Compounds, Except DAT11 Have High Potential for use as Propellant Ingredient. Isp and Detonation Properties are Computed using CHEETAH 4.0 Software. Densities Shown are from Experiments.</i></p>	
<p><b>Sensitivity with 80% AN = &gt; 60J</b></p>		

Figure 6 shows the compounds and their properties. DAT12 has very good yield (90-95%) and properties, but the impact sensitivity is below 1J. The other compounds (DAT13 to DAT17) have synthesis yields of at least 93%, and can be readily synthesized<sup>9, 10</sup>. Also they have high melting points. The most encouraging fact is that they are quite impact insensitive (more insensitive than RDX and HMX which are 7.4 J). We think that DAT13 through DAT17 polynitrogen compounds have excellent potential for use as propellants. Out of all salts considered here, DAT17 is lowest sensitivity in pure form. These compounds should be further investigated to tune the properties, such as improvement of oxygen balance. Since the energetic compounds are mixed with ammonium nitrate (AN) and a binder for formulation, we have measured impact sensitivities of each compound (DAT12 through DAT17) in varying mixtures of ammonium nitrate. Also, mixing with AN is a way to improve the insensitivity and oxygen balance. Figure 7 shows their impact sensitivities as a function of mixture composition. We have noticed dramatic improvements of impact sensitivities of all compounds in the mixtures. We, therefore, conclude that these compounds have great potential for use as propellant ingredients, and should be further investigated in Phase II.

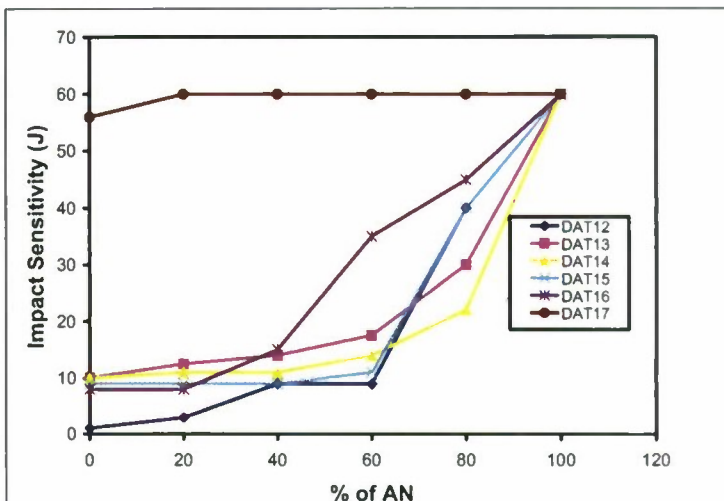


Figure 7. Impact Sensitivities of Polynitrogen Compound Mixtures as a Function AN Percent

### 3.3 Sensitivity Prediction

Impact sensitivity is the one of the most important aspects of an energetic material. An ideal energetic material should have very low impact sensitivity. While well-established theoretical techniques are available to compute/estimate heat of formation, density and specific impulse, there is no such reliable method for accurately predicting impact sensitivity. In a recent article, Keshavarz and Pouretedal<sup>11</sup> have summarized the currently available methods. A survey of these methods suggests that none of the techniques is general enough to predict impact sensitivity of an arbitrary hypothesized molecule, in particular salts. Different correlations are suggested for different classes of molecules. Therefore, impact sensitivities of molecules that do not belong to one of those classes cannot be estimated. A generalized and accurate theoretical method for impact sensitivity prediction is therefore critical to screening energetic materials from a number of hypothesized materials. Such method will have significant impact in developing new energetic materials. For example, DAT11 and DAT12 were found to have high impact sensitivity at late stage of development. Therefore, it is evident that there is a need to develop a reliable theoretical method for sensitivity prediction, in order to avoid any failure at a later stage of development. Such a model would complement other theoretical methods. Here, we have developed a preliminary model for sensitivity prediction based on Artificial Neural Network (ANN). Unlike, Quantitative Structure Property Relationship (QSPR), ANN takes in to account

the non-linearity in the prediction. In ANN, input and outputs are connected by a certain number of “hidden-layers”. Each hidden layer consists of certain number of “neurons” defined via certain functions, such as pure-linear, sigmoid etc. A set of inputs is fed into the network and a set output is produced by the network. The outputs (in this case sensitivity) are then compared with the experimental outputs and the error is calculated. The error is then minimized through the weight factors (**W** in Figure 8) until it reaches below a certain threshold using backpropagation method.

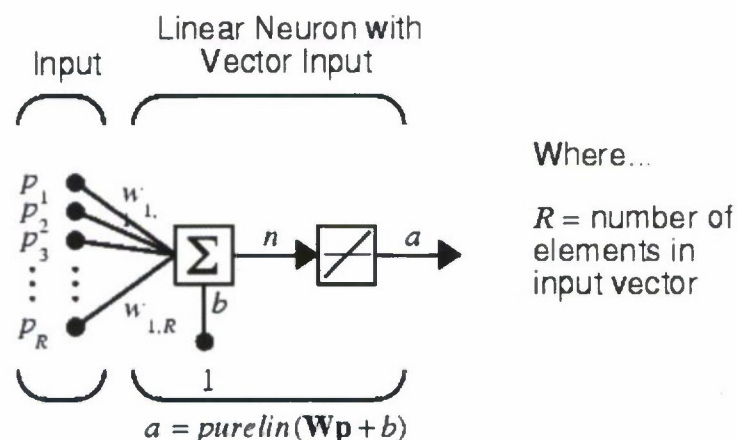


Figure 8. A Pictorial Representation of Artificial Neural Network

In the present investigation, we have used *softness*, *heat of formation*, *lowest vibrational mode*, *LUMO energy*, and *relative number of C,H,N and O atoms in the molecule* as inputs or descriptors. The softness, heats of formation, lowest vibrational modes and LUMO are quantum mechanical descriptors, and have been calculated using quantum chemical methods. The network for this work includes two hidden layers each with 5 neurons. A total of 45 molecules containing 5 and 6 membered heterocycles, and some acyclic nitramines were chosen. It should be noted that, unlike Politzer<sup>12</sup> and Keshavarz<sup>11</sup> who used different correlations for different classes of compounds, a single correlation is established with all types of compounds in this work. ANN predicts average deviation of 3.4 on H<sub>50</sub>. Only one molecule was unusually over-predicted. At this time, the reason for such deviation could not be concluded. We, however, think that there is possibility of error in experimental measurement of the data. On the other hand QSPR prediction (even without 5-membered ring compounds), although plotted in “log” scale, has much larger deviation indicating a non-linear type of relation (Figure 9). A much larger set of energetic materials will be used in Phase II to enhance the reliability of prediction.



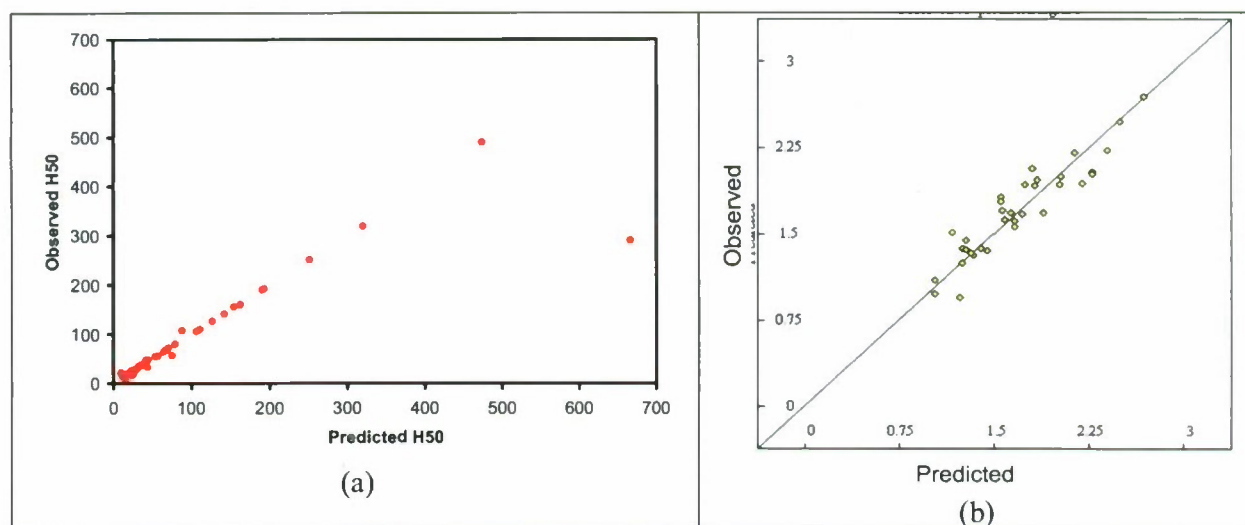


Figure 9(a). ANN Prediction; (b): QSPR LogH<sub>50</sub> Prediction without 5-membered Ring Compounds

#### 4 SUMMARY OF PHASE I WORK

Phase I work has shown the proof-of-concept that some tetrazole and amino tetrazole based energetic compounds have excellent potential to become next generation high energy propellant ingredient. Following are the summary of the Phase I work:

- A number of tetrazole based compounds have been chosen with an aim to develop high energy materials for next generation solid propellant applications.
- These compounds were evaluated theoretically for the physical and chemical properties (such as density, heat of formation, specific impulse, detonation velocity and pressure) prior to their synthesis.
- The compounds were further screened based on their anticipated difficulty level and number of steps involved in the synthesis.
- Seven compounds, most of them are salts, were synthesized and characterized for densities, melting points and impact sensitivities.
- Several of these compounds have remarkably low impact sensitivity in pure form (lower than HMX and RDX).
- Impact sensitivities of these seven compounds were further investigated in a mixture of ammonium nitrate with varying fraction. It was concluded that most of these compounds can be used as propellant ingredients along with a low percentage of ammonium nitrate. These compounds therefore deserve further investigation in the future.
- In a parallel work, we have initiated the development of an artificial neural network based model for prediction of sensitivity of energetic compounds. The preliminary work shows that it is possible to develop a single model that can predict the sensitivity of all classes of compounds.

## 5 FUTURE WORK

Although CFDRRC was not selected to write Phase II proposal, we put forward an outline of Phase II plan.

The Phase II plan is divided in to two parts: a) small scale testing of propellant formulation and further improvement of the properties of the compounds and; b) development of a comprehensive and generalized impact sensitivity predictive model that has been initiated in Phase I.

**Small Scale Propellant formulation and Testing:** The developed compounds will be further tested for electrostatic and friction sensitivity. The heat of formation of the compounds will be determined experimentally using calorimetric techniques. DSC tests will be performed to determine the thermal stability of the compounds and kinetics for reaction, if any. The compounds will be mixed with other propellant ingredients to determine any change in temperature due to mixing, since a large change in mixing temperature is undesirable. The compounds will be mixed with binders, and rheological properties will be measured. Burn rates of the pure and formulated compounds will be determined. All of the small scale (few grams level) testing has been designed to evaluate the performance of the compounds when combined with other propellant ingredients.

**Property Improvement of the Compounds:** The properties, especially oxygen balance, of these compounds will be improved via introducing oxygen rich functional groups without compromising other properties.

**Comprehensive Sensitivity Prediction Model Development:** The preliminary model developed in Phase I will be extended. The input data for ANN correlation will include more than 300 energetic compounds. The primary goal is to develop a unified model for all classes of compounds including molecular solids and salts. Since impact sensitivity data for salts are limited, extensive experimental data will be generated for salts that have already been synthesized by our university partner. Once the model is developed, it will be validated against unknown compounds. The purpose of this model development is to enable reliable prediction of impact sensitivity in order to effectively screen candidates at the early stage of development.

## 6 APPENDIX

### **Syntheses and Characterizations of the Compounds**

**DAT11:** 1,5-Diaminotetrazole (100 mg, 1 mmol) was dissolved in water (10 mL). After stirring for 10 min, methanol (10 mL) and 5-dinitromethyltetrazole<sup>1</sup> (174 mg, 1 mmol) was added, and the mixture was stirred for 12 h. The solvent was dried in air at room temperature. The yellow solid (DAT 11) was obtained in a yield of 10–20%



**DAT12:** (1,5-Diamino-tetrazolium 5-Nitro-tetrazolate (DAT12)): Compound DAT12 was prepared using water as solvent, from 1,5- diamino-tetrazole (0.010 g, 1.0 mmol) and 5-nitro-tetrazole (0.115 g, 1.0 mmol) to give a white solid in 98% yield, mp 128 °C; IR (KBr) 3344, 3267, 3099, 2861, 2660, 2482, 1713, 1634, 1542, 1507, 1446, 1426, 1371, 1321, 1186, 1161, 1125, 1078, 1006, 948, 838, 687 cm<sup>-1</sup>; <sup>1</sup>H NMR δ 6.24 (s, 2H), 6.74 (s, 2H); <sup>13</sup>C NMR δ 168.43, 153.50. Anal. Calcd for C<sub>2</sub>H<sub>5</sub>N<sub>11</sub>O<sub>2</sub> (MW 215.2): C, 11.17; H, 2.34; N, 71.62. Found: C, 11.60; H, 2.35; N, 70.87.

**DAT13:** (Bis(1,5-diaminotetrazolium) ethylene bis(5-nitroiminotetrazolate)): The reaction of 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (286 mg, 1 mmol) with 1,5-diaminotetrazole (200 mg, 2 mmol) in acetonitrile (30 mL) at reflux for 24 h gave yellow crystals of DAT13 (450 mg, 0.926 mmol, 93%) after air drying. M.p. 174 8C, 184 8C (decomp); <sup>1</sup>H NMR: d=6.93 (br. s, 10 H), 4.65 ppm (s, 4H); <sup>13</sup>C NMR: δ=154.3, 151.2, 44.6 ppm; IR (KBr): ν =1258, 1299, 1349, 1486, 1583, 1619, 1663, 3337, 3419 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>6</sub>H<sub>14</sub>N<sub>24</sub>O<sub>4</sub> (486.33): C 14.82, H 2.90, N 69.12; found: C 14.98, H 2.83, N 68.71.

**DAT14:** At 0°C, 0.030 mol cyanogen bromide was dissolved in 50 mL dry acetonitrile to which was added 0.143 mol dry sodium azide. The reaction mixture was stirred at 0 °C for 4 hours. The inorganic salt was filtered off (**Caution!** After filtering, the salt must be dissolved in cold water quickly). The solution is added to a solution containing 7 mmol 1,2-diaminoethane in 15 mL water at 0°C. After 1 day stirring at ambient temperature, the solvent was dried in air. Bis(5-aminotetrazol-1-yl)ethane<sup>2a</sup> was washed with water and acetonitrile. The yield is 71%. At 0°C, 2 mmole bis(5-aminotetrazol-1-yl)ethane was added in small portions to 10 mL 100% HNO<sub>3</sub>. The reaction mixture was stirred at ambient temperature for 18 hours. The solution was poured into 20 g ice. After stirring for 3 hours, water and nitric acid were removed in air, the product was precipitated, filtered, washed with water, and dried in air at room temperature. The yield (**DAT 14**) is 67% as a colorless crystal, which can be recrystallized from water. Colorless crystal; m.p.: 194 °C (decomposed); IR (KBr)  $\tilde{\nu}$  = 3430, 3196, 3107, 3031, 1581, 1489, 1308, 1261, 1025 cm<sup>-1</sup>; <sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, 25 °C): δ = 4.66 (s, 4H), 11.65 ppm (br. s, 2H); <sup>13</sup>C NMR ([D<sub>6</sub>]DMSO, 25 °C): δ = 44.6, 150.9 ppm; <sup>15</sup>N NMR ([D<sub>6</sub>]DMSO, 55 °C) δ = -170.6, -156.8, -154.3, -24.7, -20.1, -15.5 ppm.

**DAT15:** (1,2,4,5-Tetrazino-3,6-bis(hydrazinium) ethylene bis(5-nitroimino-1H-tetrazolate)): The reaction of 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (286 mg, 1 mmol) with 3,6-dihydrazinyl-1,2,4,5-tetrazine (142 mg, 1 mmol) in water (5 mL) at ambient temperature gave orange crystals of DAT15 (383 mg, 0.895 mmol, 89%) after air drying. M.p. 203.8C (decomp); <sup>1</sup>H NMR: d=9.63 (br. s, 8H), 4.48 ppm (s, 4H); <sup>13</sup>C NMR: d=161.4, 155.7, 43.9 ppm; <sup>15</sup>N NMR: δ=3.4, -12.7, -20.3, -31.6, -84.5, -155.1, -165.9, -289.1, -319.4 ppm; IR (KBr): ν =1262, 1298, 1328, 1357, 1431, 1475, 1498, 1555, 2097, 2739, 3013, 3215, 3443 cm<sup>-1</sup>; elemental analysis calcd (%) for C<sub>6</sub>H<sub>12</sub>N<sub>20</sub>O<sub>4</sub> (428.29): C 16.83, H 2.82, N 65.41; found: C 16.62, H 2.81, N 64.06.

**DAT16:** (Carbohydrazinium ethylene bis(5-nitroiminotetrazolate)): The reaction of 1,2-bis(5-nitroiminotetrazol-1-yl)ethane (300 mg, 1.05 mmol) with carbohydrazide (94.4 mg, 1.05 mmol) in water (6 mL) at ambient temperature gave 5 (390 mg, 1.04 mmol, 99%) as a white solid after air drying. M.p. 203.8C (decomp); <sup>1</sup>H NMR: d=8.82 (br. s, 8 H), 4.51 ppm (s, 4H); <sup>13</sup>C NMR:



d=157.3, 155.4, 44.1 ppm;  $^{15}\text{N}$  NMR:  $\delta$ =1.6, -12.9, -20.6, -89.5, -155.2, -166.1, -281.9, -321.6 ppm; IR (KBr):  $\nu$  =1034 1234, 1262, 1315, 1348, 1376, 1505, 1564, 1740, 2702, 3013, 3266, 3431  $\text{cm}^{-1}$ ; elemental analysis calcd (%) for  $\text{C}_5\text{H}_{12}\text{N}_{16}\text{O}_5$  (376.25): C 15.96, H 3.21, N 59.56; found: C 15.91, H 3.15, N 58.76.

**DAT17:** (5-Amino-tetrazolium 5-nitro-tetrazolate) Compound DAT17 was prepared using water as solvent, from 5-aminotetrazole (0.085 g, 1.0 mmol) and 5-nitro-tetrazole31 (0.115 g, 1.0 mmol) to give a white solid in 98% yield, mp 159 °C; IR (KBr) 3378, 2474, 1692, 1538, 1481, 1429, 1380, 1317, 1192, 1162, 1078, 1045, 974, 868, 833, 735, 677  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  8.30 (s, 2H);  $^{13}\text{C}$  NMR  $\delta$  168.46, 155.30. Anal. Calcd for  $\text{C}_2\text{H}_4\text{N}_{10}\text{O}_2$  (MW 200.1): C, 12.00; H, 2.01; N, 69.99. Found: C, 12.63; H, 2.07; N, 69.57.

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